

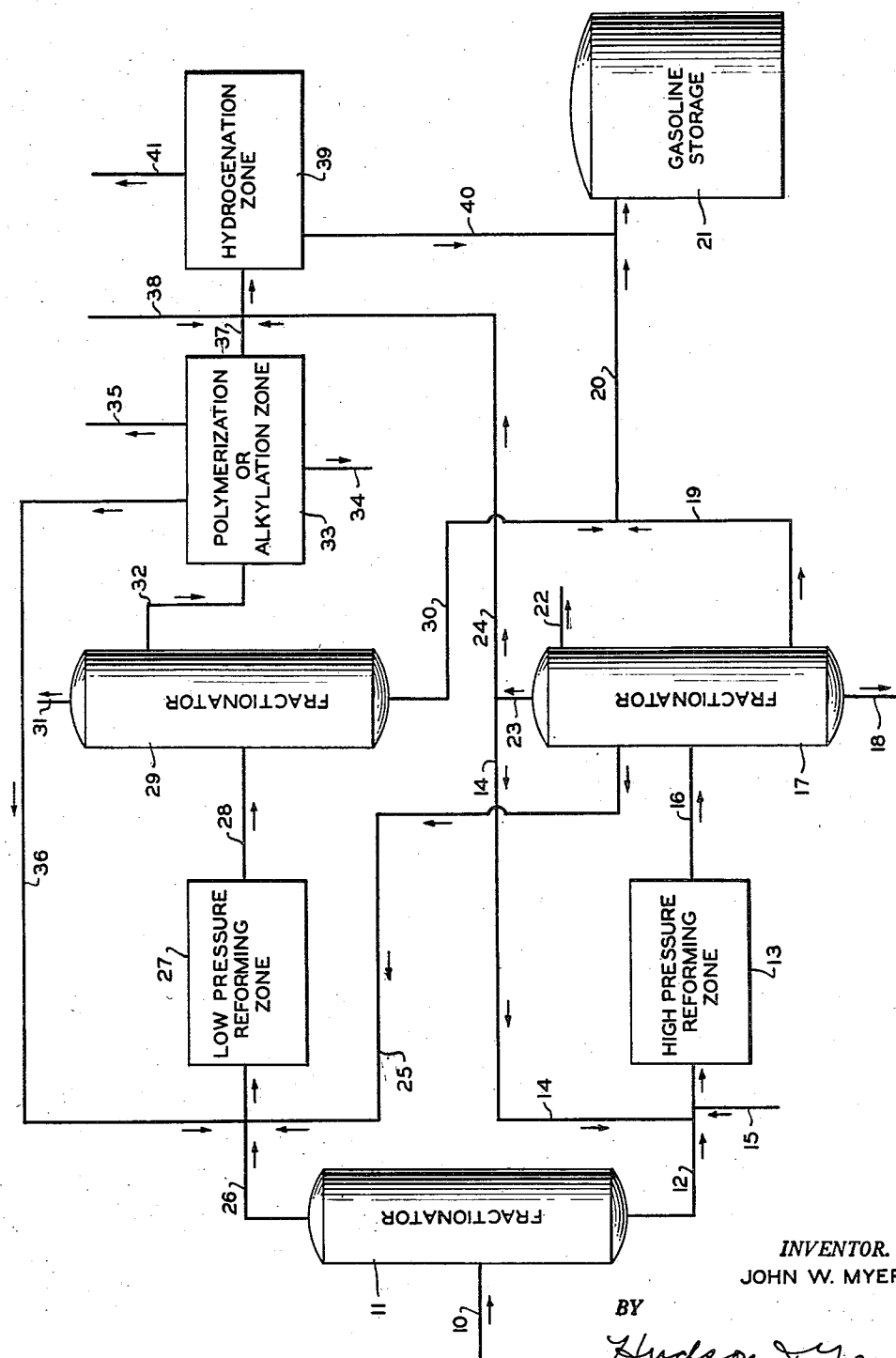
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J. W. MYERS

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CATALYTIC REFORMING PROCESS

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INVENTOR.
JOHN W. MYERS

BY

Hudson & Young
ATTORNEYS

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CATALYTIC REFORMING PROCESS

John W. Myers, Bartlesville, Okla., assignor to Phillips Petroleum Company, a corporation of Delaware

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This invention relates to the conversion of hydrocarbons. In one of its aspects it relates to a process wherein a low octane number naphtha is upgraded to produce valuable high octane motor fuels, e. g. gasoline. In another of its aspects it relates to a process wherein a low octane number naphtha is fractionated to produce a relatively heavy naphtha which is treated to produce a high octane motor fuel and a substantially saturated C₃—C₄ hydrocarbon fraction for still further treatment. In still another aspect the invention relates to a process wherein a low octane naphtha is fractionated to produce a relatively light naphtha and a relatively heavy naphtha which are then further treated under conditions optimum to each. In a still further aspect the invention relates to a process wherein the yield and quality of the gasoline produced from a low octane number naphtha are increased by more efficient utilization of the C₃ and C₄ hydrocarbons formed during the treatment of segregated fractions of an original naphtha, i. e. admixing the C₃ and C₄ hydrocarbons formed during treatment of a heavy fraction of an original naphtha, with a light fraction of said original or another naphtha and charging the mixture to a conversion step to produce a high octane motor fuel and a stream of substantially olefinic C₃ and C₄ hydrocarbons which is then further treated to produce hydrocarbons boiling within the gasoline range.

The invention has particularly satisfying application in the treatment of virgin naphthas and is for this reason so set forth and described in this application. Although all types of virgin naphthas can be used, operation is especially satisfactory when the naphthenic content in the low boiling naphtha is not excessive, say less than about 25 percent. Consequently, virgin paraffinic naphthas containing not more than 30 percent naphthenes comprise a preferred feed stock for this invention. However, the high pressure step to be described, can tolerate as high as 100 percent naphthenes. Other applications can be readily devised after a perusal of this specification and claims.

Since the advent of motor fuels of increased octane number the problem of how best to handle the relatively low octane number virgin naphthas present in nearly all crude oils has been given much attention by technologists in the petroleum industry. Various processes such as thermal reforming, catalytic reforming, hydroforming, etc. have been developed and are being used today.

The proportion of C₃ and C₄ hydrocarbons, both saturated and unsaturated, formed in these processes varies with each process and is dependent, to some extent, on the operating conditions in each. However, the relative amounts of the unsaturated and saturated hydrocarbons for each process are more or less constant. It is well known that the unsaturated C₃ and C₄ hydrocarbons are much more valuable than the corresponding saturated hydrocarbons because the unsaturated hydrocarbons can be readily converted into more valuable higher boiling hydrocarbons. Therefore, any reforming process

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which will give an increased ratio of unsaturated C₃ and C₄ hydrocarbons represents a distinct advance in the art.

I have found that when a virgin naphtha is fractionated into a relatively heavy fraction and a relatively light fraction, and each fraction catalytically reformed under optimum conditions, that the C₃ and C₄ hydrocarbons resulting from the relatively light naphtha fraction so converted are substantially olefinic in nature, whereas the C₃ and C₄ hydrocarbons from the relatively heavy naphtha fraction, so converted, are substantially paraffinic in nature. I have further found that when these paraffinic C₃ and C₄ hydrocarbons resulting from the reforming of the relatively heavy naphtha fraction are admixed with the relatively light naphtha fraction and the mixture charged to a catalytic reforming step, operated under conditions optimum for that fraction, a substantial portion of the C₃ and C₄ hydrocarbons are dehydrogenated simultaneously with the upgrading of the light naphtha to give a substantial increase in the yield of olefins which, when charged to a succeeding polymerization or alkylation operation results in a substantial increase in the yield of high octane motor fuel. The dehydrogenation of the saturated C₃ and C₄ hydrocarbons in the presence of the naphtha being reformed appears to assist in the suppression of undesirable reactions and side reactions.

Accordingly, my invention comprises fractionating a virgin naphtha into a relatively light naphtha fraction and a relatively heavy naphtha fraction, catalytically reforming the light naphtha under low pressure conditions, catalytically reforming the heavy naphtha under high pressure conditions, and admixing the C₃ and C₄ hydrocarbons from the heavy naphtha reforming step with the feed to the light naphtha reforming step to effect simultaneously a dehydrogenation of the admixed C₃ and C₄ hydrocarbons and an upgrading of the light naphtha fraction to give an increase in the yield of olefinic hydrocarbons therefrom. The olefinic C₃ and C₄ hydrocarbons from the light naphtha reforming step are then charged successively to polymerization and hydrogenation steps to give increased yields of high octane gasoline. Or, if desired, the olefinic C₃ and C₄ hydrocarbons may be charged to an alkylation step, such as alkylation of isobutane in the presence of anhydrous hydrofluoric acid.

Thus by operating according to the invention the original naphtha is more efficiently reformed and a more efficient utilization of the saturated C₃ and C₄ hydrocarbons is effected resulting in a greater yield of high octane motor fuel than is possible by methods known to the prior art.

While preferred operating conditions and hydrocarbon boiling ranges are given in the detailed description below, the invention should not be limited to those conditions because, depending upon the characteristics of the charge stock and the type of product desired, other operating conditions can be used.

For example the high pressure catalytic reforming zone can be operated at pressures ranging from 5 to 50 atmospheres, at temperatures ranging from 800 to 1150° F., at space velocities from 0.5 to 5 liquid volumes per volume of catalyst per hour, and a hydrogen circulation of from 500 to 5000 cubic feet per barrel of liquid naphtha charge.

The low pressure catalytic reforming zone can be operated at pressures ranging from 1 to 4 atmospheres, at temperatures ranging from 900 to 1150° F., and space velocities ranging from 0.5 to 5 liquid volumes per volume of catalyst per hour. Ordinarily, higher temperatures are used in the low pressure reforming zone than in

the high pressure reforming zone. The boiling ranges of the naphtha fractions charged to the zones according to the invention may vary as follows:

	ASTM Boiling Range, ° F.			
	Broad		Preferred	
	IBP	EP	IBP	EP
Total Naphtha to Operations.....	75-175	350-475	75-175	350-475
Light Naphtha to Low Pressure Reforming Zone...	75-175	185-265	75-175	200-265
Heavy Naphtha to High Pressure Reforming Zone...	185-265	350-475	200-265	350-475

Referring now to the attached diagrammatic drawing, which is one embodiment in which several of the concepts involved in this invention are illustrated a virgin naphtha having an approximate ASTM boiling range of 100-430° F. and an approximate composition of 60 percent paraffins, 2 percent olefins, 25 percent naphthenes and 13 percent aromatics, is heated in a heater (not shown) and charged through line 10 to fractionator 11. A light naphtha fraction boiling from about 100 to 230° F. ASTM is taken overhead through line 26. A heavy naphtha fraction boiling from about 230 to 430° F. ASTM is withdrawn from fractionator 11 through line 12, through a vaporizing heater (not shown) to high pressure reforming zone 13. Hydrogen can be added through lines 14 and 15. Typical or preferred operating conditions for reforming zone 13 are: temperature 900-1000° F., pressure 10 to 25 atmospheres, space velocity 0.8 to 3 liquid volumes per volume of catalyst per hour and hydrogen, 1000 to 3000 cubic feet per barrel of liquid naphtha charge to said zone.

The converted heavy naphtha vapors are passed through line 16 to fractionation zone 17 wherein the normally liquid hydrocarbons are separated from the normally gaseous hydrocarbons. The heavy end liquid residue boiling above the gasoline range is withdrawn through line 18, the gasoline fraction is passed through lines 19 and 20 to gasoline storage 21, residue gas, largely C₁ and C₂ hydrocarbons, is taken overhead through line 22 and the hydrogen rich gas is taken overhead through line 23 for recycle through line 14 or transfer through line 24 to the hydrogenation zone to be described below. The C₃ and C₄ hydrocarbons (substantially saturated) are withdrawn through line 25 and admixed with the light naphtha fraction in line 26.

The light naphtha fraction in line 26 is that taken overhead from fractionator 11. These light naphtha vapors, after admixture with the substantially saturated C₃ and C₄ hydrocarbon vapors from the high pressure catalytic reforming zone 13, are passed to low pressure catalytic reforming zone 27 wherein the C₃ and C₄ hydrocarbons are substantially dehydrogenated, forming free hydrogen in the said zone, while portions of the light naphtha hydrocarbons are being simultaneously upgraded. Typical or preferred operating conditions in low pressure catalytic reforming zone are: temperature 950 to 1075° F., pressure 1 to 3 atmospheres, space velocity 1 to 3 liquid volumes per volume of catalyst per hour. Additional hydrogen (not shown) can be added to the feed to decrease the formation of coke. However, the proportion of added hydrogen should be adjusted in view of the dehydrogenation reactions.

The reformed naphtha constituents and dehydrogenated C₃ and C₄ hydrocarbons are passed through line 28 to fractionation zone 29 to separate the gasoline fraction from the lighter vapors. The gasoline fraction is withdrawn through line 30 and passed through line 20 to gasoline storage 21. Part or all of the residue gas is taken overhead through line 31. The substantially ole-

finic C₃ and C₄ hydrocarbons are passed through line 32, together with some or all of the light gases from fractionation zone 29, to polymerization zone 33 (preferably catalytic) wherein the said olefins are polymerized to higher boiling hydrocarbons. The heavier liquid from polymerization zone 33 is withdrawn through line 34, residue gas is taken overhead through line 35 and unpolymerized hydrocarbons are withdrawn through line 36 for recycle to the low pressure catalytic reforming zone. By controlling conditions in polymerization zone 33, as well as the proportion of gases introduced thereto through line 32 or some other source not shown, the character and extent of the polymerization reaction effected in polymerization zone 33 can be controlled flexibly as a further feature of this invention. The polymerized hydrocarbons are withdrawn through line 37, admixed with hydrogen from an outside source through line 38 or system hydrogen from line 24 and the resulting mixture passed to hydrogenation zone 39. The hydrogenated reaction product is withdrawn through lines 40 and 20 to gasoline storage 21. Residue gas containing hydrogen is taken overhead through line 41. The hydrogen therein can be recovered and recycled if desired.

Any effective hydrogenation catalyst and correspondingly suitable hydrogenating conditions known to the art may be employed in hydrogenation zone 39. Likewise, any suitable polymerization catalyst such as silica-alumina, copper pyrophosphate, phosphoric acid, sulfuric acid etc. and suitable operating conditions known to the art may be employed in polymerization zone 33. Catalysts which can be employed in the low pressure and the high pressure catalytic reforming zones include the chromia-alumina type, molybdena-alumina type etc. and also platinum-containing catalysts, all well known to those skilled in the art.

The following examples illustrate the advantages of my invention as explained at each example. Example I shows that it is more desirable to reform the light naphtha at low pressures than at high pressures. Example II shows that the use of high pressure is desirable when reforming a heavy naphtha. Example III shows that the C₃ and C₄ hydrocarbons resulting from the reforming of light naphtha at low pressure contain a substantial amount of olefins whereas the C₃ and C₄ hydrocarbons from the reforming of heavy naphtha are substantially paraffinic and contain only a small amount of olefins. Example IV shows that substantial portions of saturated C₃ and C₄ hydrocarbons passed through a low pressure catalytic reforming zone will be dehydrogenated and Example V shows that this dehydrogenation will be effected simultaneously in the presence of a naphtha which is upgraded in such an operation.

Example I

CATALYTIC REFORMING OF LIGHT NAPHTHA BOILING RANGE 100-263° F. ASTM

	Feed	Low Pressure	High Pressure
Temperature, °F.....		998	994
Pressure, atm.....		1	21
Hydrogen, Mol/mol of feed.....		2.0	2.3
Space velocity, liq. vol./cat. vol./hr.....		3.0	2.7
Yield of C ₃ +, wt. percent of feed (Gasoline boiling range).....		92.0	78.7
Yield of Coke, wt. percent of feed.....		0.25	0.03
Octane rating of C ₃ +(gasoline):			
Motor+1.0 ml. TEL.....	76.3	81.6	79.6
Research+1.0 ml. TEL.....	76.4	86.1	82.2
Catalyst Used.....		(1)	(1)

¹ Chromia-alumina.

A comparison of the data at the bottom of columns 2 and 3 shows that both a greater yield of the C₃+ fraction (corresponding to gasoline) and a greater improvement in octane number thereof were obtained at the low pressure conditions than at the high pressure conditions.

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Example II

CATALYTIC REFORMING OF HEAVY NAPHTHA
BOILING RANGE 230-415° F. ASTM

	Feed	Low Pressure	High Pressure
Temperature, °F.....	-----	940	929
Pressure, atm.....	-----	1.7	17.0
Hydrogen, Cu. ft./barrel.....	-----	2,400	2,400
Space velocity, liq. vol./cat. vol./hr.....	-----	0.95	0.97
Yield of C ₃ +, wt. percent of feed.....	-----	91	83
Yield of coke, wt. percent of feed.....	-----	2.4	0.8
Octane rating of C ₃ +(gasoline) Motor, clear.....	28.2	52.2	70.0
Catalyst used.....	-----	(¹)	(¹)

¹ Molybdena-alumina.

These data show that the "high pressure" conditions are desirable for this feed stock. It should be noted in column 3 that the octane number of the gasoline formed is 70.0 and the yield of coke is 0.8 percent for the high pressure operation compared to an octane number of 52.2 and a coke yield of 2.4 percent for the low pressure operation shown in column 2. The C₃+ fraction (gasoline) obtained under the low pressure conditions would of necessity require further treatment to increase the octane rating to a satisfactory value.

Example III

CATALYTIC REFORMING OF LIGHT NAPHTHA AND
HEAVY NAPHTHA

Naphtha Fraction.....	Light Naphtha			Heavy Naphtha		
Boiling Range of Naphtha, ° F., ASTM.....	94-227			230-415		
Pressure, atm.....	1.7			17.7		
Temperature, ° F. (approx.).....	1,060			959		
H ₂ , Cu. ft./bbl.....	660			2,560		
Space Velocity, Liq. vol./cat. vol. hr.....	2.48			0.98		
Products, wt. percent:						
Hydrogen.....	0.9			0.8		
Methane.....	2.1			1.7		
Ethylene.....	1.6			trace		
Ethane.....	1.0			3.2		
Propylene.....		1.1			0.3	
Propane.....			0.6			4.1
Isobutylene.....		0.3				
n-butene.....		1.5				
Butenes.....					0.4	
Isobutane.....			0.1			
n-butane.....			0.8			3.9
Debutanized gasoline.....	89.1			82.9		
Coke.....	0.9			0.3		
Loss.....	0.0			2.4		
Sub-totals.....	95.6	2.9	1.5	91.3	0.7	8.0
Total.....	100.0			100.0		
Catalyst Used.....	Chromia-alumina			Chromia-alumina		

These data show that in the low pressure catalytic reforming of the light naphtha 65.9 percent of the C₃ and C₄ hydrocarbons are olefinic whereas only 8.0 percent of the C₃ and C₄ hydrocarbons formed during the high pressure catalytic reforming of the heavy naphtha are olefinic.

Example IV

DEHYDROGENATION OF C₃ AND C₄ HYDROCARBONS

Dehydrogenation of.....	Propane	Butane
Space velocity, gaseous vol./cat. vol./hr.....	700	769
Temperature, ° F.....	1,100	1,080
Pressure, atm.....	1.5	1.0
Percent converted to propylene.....	37	-----
Percent converted to unsaturated C ₃ and C ₄ Hydrocarbons.....	-----	43
Catalyst.....	(¹)	(¹)

¹ Chromia-alumina.

Example V

A mixture comprising 8.1 weight percent of normal butane and 91.9 weight percent of normal hexane concentrate was charged over a chromia-alumina catalyst at

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atmospheric pressure, 979° F., and a space velocity of 1.8 liquid volumes per volume of catalyst per hour. The butane was dehydrogenated to the extent that the butane, butene, and hydrogen in the product were substantially at equilibrium concentrations.

Various other naphthas such as naphthas from naphthenic or aromatic type crudes, naphthas resulting from the cracking of topped crude, etc., may also be treated according to the invention. Also, in some cases, it may be desirable to charge propane and butane from an external source to the low pressure reforming step in addition to, or instead of, the C₃ and C₄ hydrocarbons from the high pressure reforming step. Such operation is within the scope of the invention.

While the invention has been described as a process wherein a naphtha is fractionated into a light naphtha fraction and a heavy naphtha fraction, with the fractions being catalytically reformed under conditions optimum to each and the substantially saturated C₃ and C₄ hydrocarbons formed in the heavy naphtha reforming step being passed to the light naphtha reforming step it is obvious that other embodiments are within the scope of the invention.

For example, an original naphtha can be fractionated into a plurality of fractions, the individual fractions catalytically reformed under conditions optimum to each and the substantially saturated C₃ and C₄ hydrocarbons formed in one or more of the heavy naphtha reforming steps being passed to one or more of the light naphtha reforming steps. In such a process operating conditions for the individual catalytic reforming steps will vary with the boiling range of the naphtha fraction and in accordance with the above-detailed description of the invention, i. e., the heaviest naphtha will be reformed at the highest pressure and the lightest naphtha at the lowest pressure. Obviously the number of light fractions and the number of heavy fractions into which an original naphtha is fractionated will depend upon the properties of the original naphtha and the type of products desired therefrom. In some instances it may be desirable to segregate only one light naphtha fraction and two or more heavy fractions or, in other instances, one heavy fraction and two or more light fractions, from an original naphtha for treatment in accordance with the invention.

Variations and modifications are possible within the scope of the foregoing disclosure, drawing, and appended claims to the invention, the essence of which is a catalytic reforming process comprising, fractionating a low octane number naphtha into a light naphtha and a heavy naphtha, catalytically reforming each fraction under conditions optimum to each, and admixing the C₃ and C₄ hydrocarbons from the heavy naphtha reforming step with the feed to the light naphtha reforming step to increase the yield of olefinic hydrocarbons therefrom; and further, passing the olefinic C₃ and C₄ hydrocarbons formed in said light naphtha reforming step to a further treating step to convert the said olefins into more valuable hydrocarbons. In this manner the yield of high octane gasoline from a given naphtha is increased.

I claim:

1. A process for treating a relatively low octane number naphtha which comprises, fractionating said naphtha into a plurality of fractions ranging from light naphtha to heavy naphtha, catalytically reforming each said fraction under conditions optimum to each, and admixing C₃ and C₄ hydrocarbons formed in at least one of the said heavy naphtha fraction reforming steps with the feed to at least one of the said light naphtha fraction reforming steps to form a mixture consisting essentially of said light naphtha fraction and said C₃ and C₄ hydrocarbons, passing said mixture to a light naphtha catalytic reforming zone and therein simultaneously upgrading said light naphtha and dehydrogenating said C₃ and C₄ hydrocarbons to form corresponding olefins.

2. A process for treating a relatively low octane num-

ber naphtha which comprises, fractionating said naphtha into a light naphtha and a heavy naphtha, passing said heavy naphtha to a catalytic reforming zone wherein the said heavy naphtha is vaporized and contacted with a reforming catalyst in the presence of hydrogen under high pressure conditions, fractionating the products from said heavy naphtha reforming step into a plurality of fractions including a fraction boiling within the gasoline range and a fraction comprising substantially saturated C₃ and C₄ hydrocarbons, admixing said C₃ and C₄ hydrocarbons with the said light naphtha fraction to form an admixture consisting essentially of said light naphtha fraction and said C₃ and C₄ hydrocarbons, contacting the said admixture with a reforming catalyst in a light naphtha catalytic reforming zone operated under low pressure conditions, and therein simultaneously upgrading portions of the light naphtha and dehydrogenating portions of the C₃ and C₄ hydrocarbons contained in said admixture in the said low pressure catalytic reforming zone.

3. The process of claim 2 wherein the said high pressure conditions comprise a temperature within the range of 900 to 1000° F., a pressure within the range of 10 to 25 atmospheres, a space velocity within the range of 0.8 to 3 liquid volumes per volume of catalyst per hour and hydrogen volume within the range of 1000 to 3000 cubic feet per barrel of naphtha; and the said low pressure conditions comprise a temperature within the range of 950 to 1075° F., a pressure within the range of 1 to 3 atmospheres and a space velocity within the range of 1 to 3 liquid volumes per volume of catalyst per hour.

4. A process for treating a low octane number naphtha which comprises: fractionating said naphtha into a relatively light naphtha and a relatively heavy naphtha; catalytically reforming the heavy naphtha fraction under conditions to obtain substantially saturated C₃ and C₄ hydrocarbons in the effluent from the heavy naphtha reforming zone; fractionating said effluent to separate said C₃ and C₄ hydrocarbons therefrom; admixing said C₃ and C₄ hydrocarbons formed in said heavy naphtha reforming zone with said light naphtha to form a mixture consisting essentially of said light naphtha and said C₃ and C₄ hydrocarbons; passing said mixture to a light naphtha catalytic reforming zone and therein simultaneously upgrading said light naphtha and dehydrogenating said C₃ and C₄ hydrocarbons to form corresponding olefins.

5. A process for treating a low octane number naphtha which comprises: fractionating said naphtha into a relatively light naphtha fraction and relatively heavy naphtha fraction; catalytically reforming said heavy naphtha fraction under high pressure conditions in a catalytic reforming zone to obtain substantially saturated C₃ and C₄ hydrocarbons in the effluent from said heavy naphtha reforming zone; fractionating said effluent to separate said C₃ and C₄ hydrocarbons therefrom; admixing said separated C₃ and C₄ hydrocarbons formed in said heavy naphtha reforming zone with said light naphtha fraction to form a mixture consisting essentially of said light naphtha and said separated C₃ and C₄ hydrocarbons; passing said mixture to a light naphtha catalytic reforming zone operated at a temperature within the range of 950 to 1075° F., and a pressure within the range of 1 to 3 atmospheres, and therein simultaneously upgrading said light naphtha and dehydrogenating said C₃ and C₄ hydrocarbons to form corresponding olefins.

6. A process according to claim 5 wherein said high pressure conditions in said heavy naphtha reforming zone comprise a temperature within the range of 900 to 1000° F., and a pressure within the range of 10 to 25 atmospheres.

7. A process according to claim 6 wherein said light naphtha has a boiling range within the range of 75 to 265° F. and said heavy naphtha has a boiling range within the range of 185 to 475° F.

8. The process of claim 7 wherein the catalyst employed in said light naphtha catalytic reforming is chromia-alumina and the catalyst employed in said heavy naphtha catalytic reforming is selected from the group consisting of chromia-alumina and molybdena-alumina.

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